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Dynamic Mechanical Properties of Poly(γ-benzyl L-α-glutamate) Gels in Benzyl Alcohol

A. K. Murthy[†] **and M. Muthukumar***

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003. *Received July 23, 1986*

ABSTRACT: The dependencies of the loss and storage moduli of solutions of poly(γ-benzyl L-glutamate) in benzyl alcohol on temperature, composition, and frequency are reported. It is found that the rheological behavior of the gel phase is dominated by kinetics and strongly depends on whether the gel is prepared from the high-temperature isotropic phase, biphasic phase, or the liquid crystalline phase.

Introduction

The growing demand for high-modulus fibers has resulted in the recent upsurge in the synthesis and production of liquid crystalline polymers. Due to their rigidity, rigid rodlike polymers tend to retain good orientation during spinning into fibers. In solution spinning, the polymer solution is extruded through a spinneret and the fibrils are drawn through a bath, called a coagulation bath, wherein the most important phenomenon, gelation, occurs. The strength of the fibers depends upon the gelation conditions.[1] Gelation is also an important phenomenon in many biological systems.[2-7] There are two distinct types of gels. In one, all the cross-links are chemically cross-linked and hence are permanent. In the other, the junction points are mobile in the sense that these cross-links will be continuously formed by physical entanglements and deformed. These physical cross-links make the gels thermoreversible, with the name suggesting that these gels go into solution on heating and the network is re-formed on cooling. In this work, we mainly focus our attention on such gels formed by the synthetic polypeptide poly(γ-benzyl L-α-glutamate) (PBLG) in the helicogenic solvent benzyl alcohol (BA).

The classic picture for the phase diagram of rigid rod polymers in solution is due to Onsager[8] and Flory,[9] showing three distinct phases depending upon the temperature and concentration (Figure 1). At sufficiently low concentration and high temperature, the solution is in the isotropic phase. Between the concentrations corresponding to the Robinson A[10,11] and the Robinson B[10,11] points and at high temperatures, the solution is in the narrow biphasic phase, wherein the isotropic and the liquid crystalline phases coexist. Beyond the concentrations corresponding to the Robinson B point and at high temperatures, the solution is in the pure liquid crystalline phase. At lower temperatures, all the phases go into the so-called wide biphasic phase. It is in this phase that the above-mentioned gelation occurs. Experimental results for the phase diagram for some rigid rodlike polymers in solution agree qualitatively[12,13] with Flory's theory, but many researchers have questioned the use of Flory's theory as a quantitative measure because of the assumptions involved in the development of the theory.[14] The effect of side-chain flexibility on phase equilibria was included in Flory's theory by Wee and Miller,[15] and later Flory and co-workers[16-22] incorporated polydispersity into their theoretical model to study its effect on the phase equilibrium. Miller et al.[12,13,15,23-27] made extensive studies on PBLG in various other solvents to arrive at the correct phase diagram based on their optical microscopic observations and their measurements of cholesteric pitch as a function of temperature by static light scattering. Sasaki et al.[28,29] and Ginzburg et al.[30] investigated the phase diagram for the PBLG–BA and PBLG–DMF systems, respectively. More basic than determining the phase boundaries are the questions concerning the definition and identification of the gel phase and the molecular origins of such a phase. These fundamental questions and the added complexity of the dynamics in each phase pose considerable difficulties to the successful development of a good theory that can describe the dynamics of such polymers in all phases. In this work, we attempt to make a systematic study of each phase for one such system, PBLG in benzyl alcohol, with the aim of understanding the dynamical behavior in each phase by performing oscillatory shear experiments. For this system, the isotropic and cholesteric phases are separated by a narrow biphasic region at higher temperatures. As the temperature is lowered, a gel phase is formed at all concentrations. Our goal is to establish the boundaries of the gel phase and to understand the nature of the gel phase.

Experimental Section

PBLG was purchased from Sigma Chemicals and the solutions were prepared by weighing the polymer and the solvent. The concentrations are expressed as weight percentage. The polymer (MW = 345 000) was dissolved by heating the solution to 70 °C with mechanical stirring. Rheological measurements were performed on a Rheometrics dynamical spectrometer fitted with parallel plates of 25-mm diameter. For the sinusoidal deformation, the applied stress (σ) and the strain (γ) are related by[31]

$$\sigma = \gamma[G' \sin(\omega t) + G'' \cos(\omega t)] \qquad (1)$$

[†] On leave from the Department of Chemistry, Sri Krishnadevaraya University, Anantapur, India 515 003.

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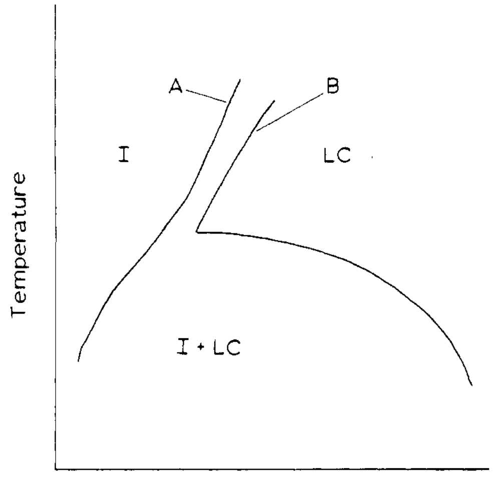

Figure 1. Typical phase diagram for a rigid rod polymer solution (not drawn to scale) indicating all three phases: isotropic (I), liquid crystalline (LC), and biphasic (I + LC). *A* and *B* are the concentrations corresponding to the Robinson A and B points, respectively.

Here, G' is the storage modulus, G'' is the loss modulus, and ω is the deformation frequency. The complex viscosity, η^*, is given by

$$\eta^* = [(G'/\omega)^2 + (G''/\omega)^2]^{1/2} \qquad (2)$$

A polymer solution of a given concentration was poured on the lower parallel plate of the Rheometrics dynamical spectrometer, and the upper plate was then lowered slowly until the solution spread evenly between the parallel plates, with sufficient care being taken not to trap any air bubbles in the sample. The plates, which were enclosed in an environmental chamber, were then heated to 70 °C and allowed to stand for about 5–10 min. This allows the system to reach thermal equilibrium and ensures loss of any thermal history. For isotropic solutions (i.e., solutions below the Robinson A point), we tried initially to measure the storage modulus as a function of frequency, by allowing the sample between the plates to cool to room temperature from 70 °C at a rate prescribed on the spectrometer. These attempts to measure the rigidity of the gel from isotropic solutions resulted in moduli that decreased on successive measurements on the same gel at a small strain (1%). Aging for 24–36 h at room temperature, after cooling to room temperature from 70 °C, also resulted in a high value for the storage modulus at the first time of measurement, and the same decreased to half of its original value by the end of our third successive measurement taken on the same sample. Only after repeated (3–4 times) heating and cooling cycles, could we succeed in producing reproducible results for the material functions.

This kind of heat treatment is good for measuring the moduli in the gel phase only if one goes directly to the gel phase from the isotropic solution phase. Instead, we decided to study the viscoelastic behavior at all temperatures and concentrations that include all three phases in the phase diagram for the PBLG–BA system, with the aim of examining how the ultimate elastic properties of the gels prepared reflect their high-temperature (solution) behavior. Here, we had to follow a different heat treatment to get reliable results for the viscoelastic properties. At high temperatures and concentrations between the Robinson A and B points, the dynamics of the polymer chains, complicated by the kinetics of phase separation into the isotropic and liquid crystalline phases, presented an additional problem in that at least 6–9 h was required for the moduli to reach a fairly steady value at a given frequency and strain. Because of this time dependence, we treated all our samples between the parallel plates for a fixed time at a given temperature, with the upper plate oscillating at a fixed frequency and amplitude as described below. Thus, separate gelations are performed at each temperature. With this time and heat treatment, we measured the viscoelastic response to a given cycle of deformation from various concentrated samples of PBLG in benzyl alcohol, covering all three phases. The results thus obtained at various concentrations and temperatures are discussed in the next section.

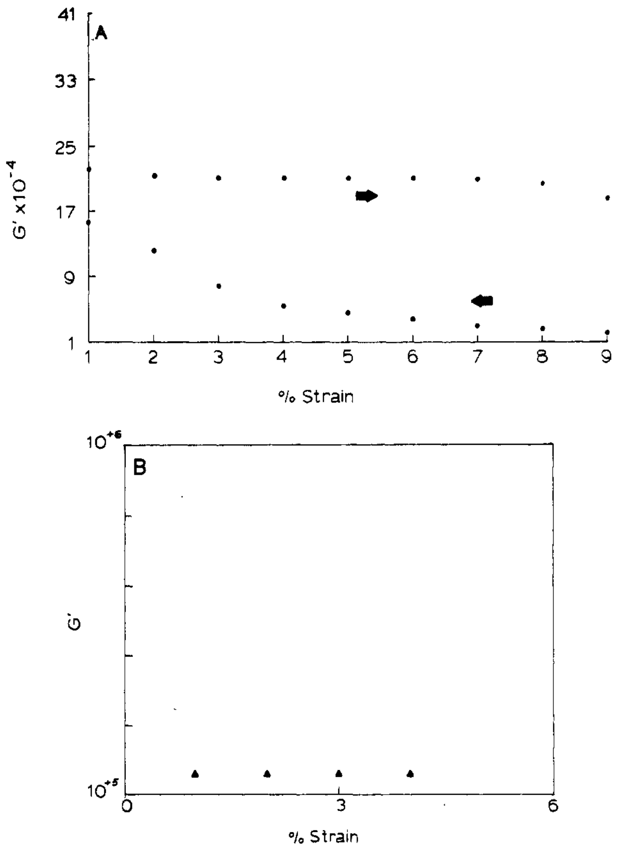

Figure 2. (A) Storage modulus (G')–strain hysteresis loop for PBLG–BA gel. Concentration = 1%, T = 25 °C, and ω = 1 rad/s. G' is in units of dyn/cm^2. (B) Linear viscoelastic regime for PBLG–BA gel, with repeated measurements superimposing. Concentration = 1%, T = 25 °C, and ω = 1 rad/s. G' is in units of dyn/cm^2.

Results and Discussion

A. Gelation Temperatures. The linear viscoelastic regime, at all concentrations and temperatures, is found to be restricted to very small strain levels (up to 3% strain). After the sample was subjected to an oscillatory shear at a frequency of 1 rad/s up to a level of 10% strain, the experiment was repeated with strain decreasing from 10% to 1%. This resulted in a hysteresis loop (Figure 2A). For strain levels less than 3%, repeated measurements gave exactly the same values for the material functions (Figure 2B). In the present study, the gelation temperatures are determined by monitoring the gradual buildup of storage modulus on going from solution to the gel state by approximately identifying the inflection point. This change is sharper in going from the isotropic to the gel state (i.e., at low concentrations) (Figure 3A) than in going from the anisotropic cholesteric phase to the gel state (i.e., at high concentrations) (Figure 3B).

The main interest in determining the gelation temperature is to arrive at a phase diagram for the PBLG–BA system by identifying the gelation temperature as the temperature corresponding to the transition of the isotropic or anisotropic phase into the gel phase. The phase diagram obtained in this way is presented in Figure 4. The narrow biphasic region at high temperatures is shown by broken lines because of the difficulties involved in the precise determination of its phase boundaries.

B. Frequency Dependence. As pointed out in the Experimental Section, the storage modulus exhibits a time dependence. It is observed to take several hours for the

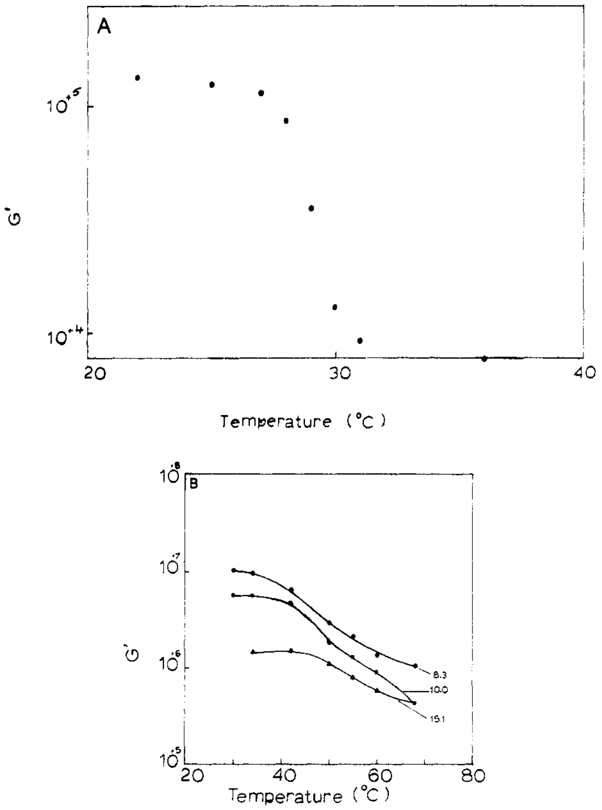

Figure 3. Dependence of the storage modulus increase on the high-temperature phase of the solutions from which the gels are prepared ($\omega = 1$ rad/s, $\gamma = 1\%$). G' is in units of dyn/cm^2. (A) From isotropic solution (concentration = 1%) to the gel phase; (B) from the narrow biphasic and liquid crystalline phases to the gel phase. The numbers against the curves indicate the concentrations in weight percent.

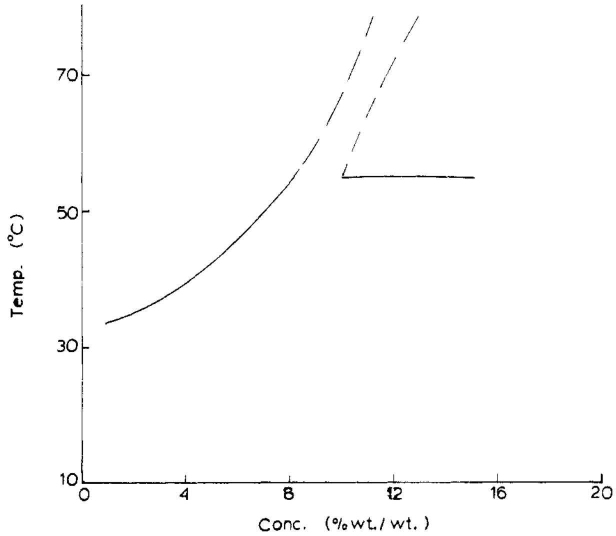

Figure 4. Phase diagram obtained from the gelation temperature measurements for PBLG–BA solutions.

storage modulus to reach a limiting value, requiring longer times at higher concentrations. Reproducing the data for the same sample became difficult due to the dependence of the moduli on time. To overcome this time dependence, we followed a fixed time schedule at every temperature. After melting the sample between the parallel plates of the rheometer at 70 °C, we started the experiment at 68 °C by subjecting the sample to an oscillatory deformation at $\omega = 1$ rad/s and $\gamma = 1\%$. The time evolution of the moduli was then recorded, and Figure 5 illustrates this for a 10% solution. The time required to reach a steady value is

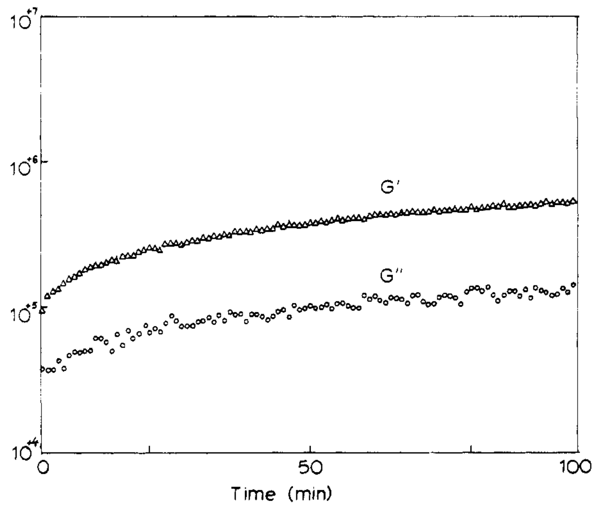

Figure 5. Typical picture showing the time evolution of the storage (G') and loss (G'') moduli (in dyn/cm$_2$) for PBLG–BA solutions. Concentration = 10%, T = 68 °C, $\omega = 1$ rad/s, and $\gamma = 1\%$.

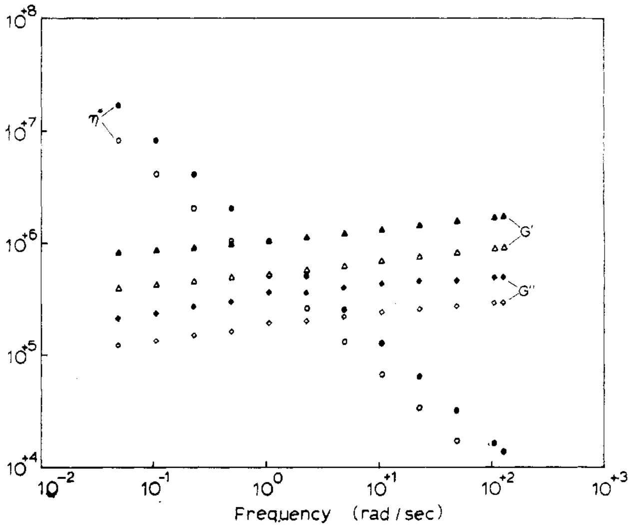

Figure 6. Effect of time on the material functions for PBLG–BA solutions. The filled points represent the material functions measured after 3 h from the initial measurement (open points). Concentration = 8.3%, T = 68 °C, $\omega = 1$ rad/s, and $\gamma = 1\%$. The moduli G' and G'' are in units of dyn/cm^2 and the complex viscosity η^* is expressed in poise.

taken as the fixed time for this temperature, and similarly the times required at all other temperatures were determined. Thus we arrive at a time schedule for each temperature and the *same* time schedule was followed for all samples of various concentrations at that temperature. With true equilibrium taking much longer times (days to weeks), this kind of temperature–time schedule allows one to study the system at a stage close to the true equilibrium. It is evident from Figure 6 that the effect of time (reaching real equilibrium) is to change the material functions quantitatively, leaving unaffected the qualitative behavior at all frequencies of deformation. Accordingly, we believe that the conclusions drawn (see below) from measurements taken under this time schedule are valid for the system under real equilibrium (i.e., the system at infinite time).

The spectra of G', G'', and η^* as functions of frequency, with oscillating deformation of small amplitude to maintain the linear behavior, are shown in Figures 7–9 for a solution of 8.3 wt%. Very little dependence of G' and G'' on frequency and the fact that G' is higher than G'' prove the elastic nature of PBLG solutions in benzyl alcohol. At

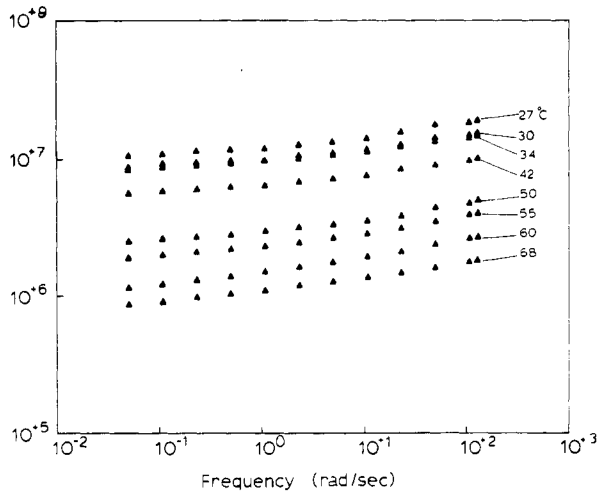

Figure 7. Frequency dependence of the storage modulus G' (in dyn/cm^2) at various temperatures shown for an 8.3% solution of PBLG in benzyl alcohol. $\gamma = 1\%$.

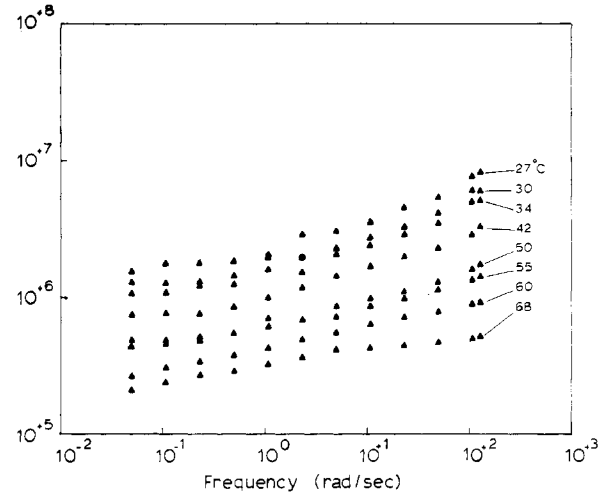

Figure 8. Frequency dependence of the loss modulus G'' (in dyn/cm^2) for the same conditions as in Figure 7.

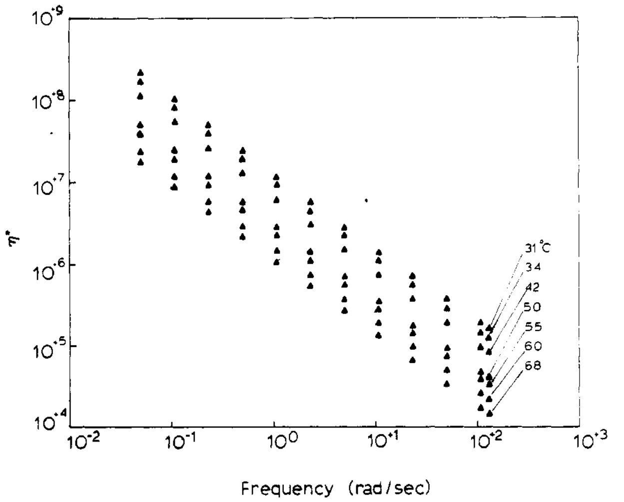

Figure 9. Complex viscosity η^* (in poise) for PBLG solutions in benzyl alcohol for the same conditions as in Figure 7.

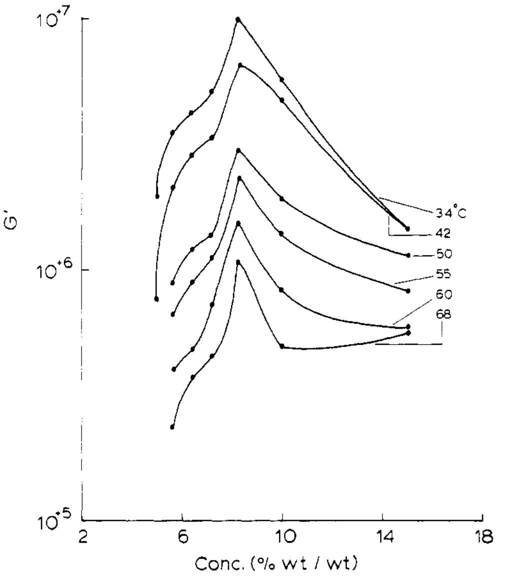

Figure 10. Dependence of the storage modulus G' (in dyn/cm^2) on concentration, covering all three phases of the PBLG–BA system. $\omega = 1$ rad/s and $\gamma = 1\%$.

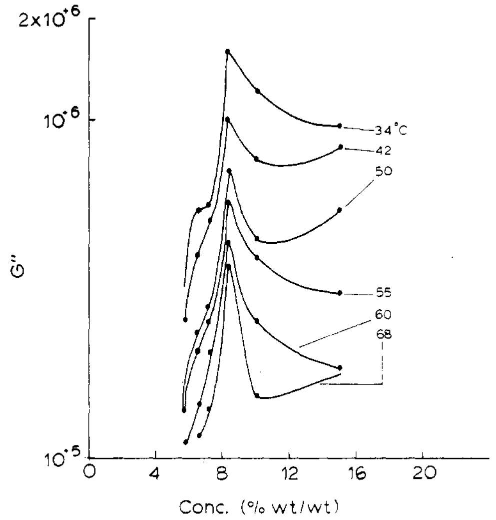

Figure 11. Concentration dependence of the loss modulus G'' (in dyn/cm^2) for the same conditions as in Figure 10.

all temperatures studied, G' and G'' show the same dependency on frequency, suggesting that the sample retains high-temperature structure even at lower temperatures. The complex viscosity decreases with frequency according to the scaling law $\eta \sim \omega^{-1}$. The real component of the complex viscosity, η' ($=G''/\omega$), decreases with frequency as ω^{-1}, reaching no limiting value at lower frequencies. This is in contrast to the behavior of PBLG in *m*-cresol[32] and Kevlar in H_2SO_4.[33]

The response of G' and η' to frequency is more like a "solid" response, typically observed for concentrated polymer solutions and permanently cross-linked gels.[31] One reason may be that the time scale employed even at the lowest frequency may not be sufficient for the entanglements to disentangle and flow. Because of the limitation of the apparatus, we could not go to much lower frequencies to look for a limiting value for the real component of the complex viscosity. Since we observe the same behavior at all temperatures, including the gel phase, we believe that orientation relaxation[34] plays a dominant role within the time scale of measurement.

C. Concentration Dependence. As shown in Figures 10 and 11, the storage and loss moduli increase with concentration up to a certain concentration and then decrease with further increase in concentration with a shoulder on the lower concentration side. Starting with the classic work by Hermans,[35] many others observed a peak in shear viscosity and/or dynamic viscosity–concentration curves.[32,33,35-37] Following Hermans, it is customary to

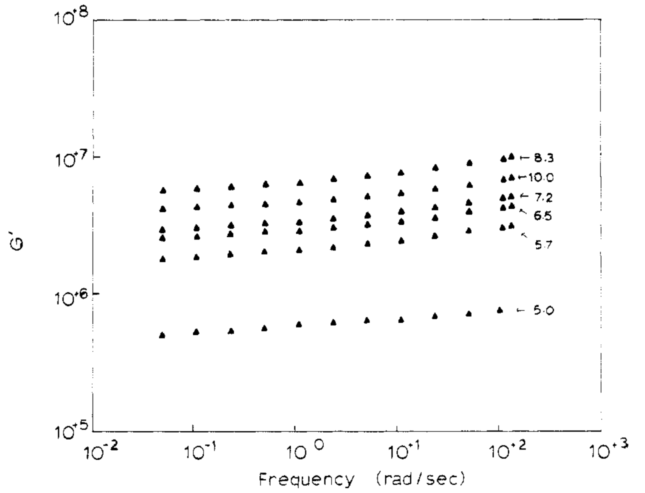

Figure 12. Concentration dependence of the storage modulus G' (in dyn/cm^2), showing the same concentration dependency at all frequencies of deformation. The numbers against the curves indicate the concentrations in weight percent. T = 42 °C, γ = 1%.

identify the concentration at which the viscosity is maximum as the concentration corresponding to the narrow biphasic region in the phase diagram of the respective rigid rod polymer–solvent system.

To the left of the peak in Figure 10, we observe a shoulder at all temperatures. Similar behavior has also been observed for other systems.[32,36] Aharoni[36] observed a shoulder to the left of the viscosity maximum for the polyisocyanate–toluene system, while Kiss and Porter[32] noted a shoulder to the right of the storage modulus maximum for PBLG in *m*-cresol. In the present study, we observe a shoulder on the lower concentration side. On the basis of optical microscopic observations and some empirical calculations, Aharoni argued that the presence of the shoulder was an indication of the liquid crystalline phase dispersed in the isotropic matrix. To understand this more thoroughly, we are currently performing quasi-elastic light scattering studies under the same conditions as covered in this rheological study. At concentrations higher than the peak concentration, there is a smooth decrease of moduli with concentration at temperatures above 50 °C, while there is a steeper decrease at temperatures below 50 °C.

Sasaki et al. have also studied the dependence of the elasticity of PBLG–BA gels on temperature and concentration using a free-oscillating torsion pendulum with concentric cylinders. Our results are consistent with the data of Sasaki et al. However, they restricted their investigation to gels of concentrations from 0.1 to 8 wt % and consequently they did not observe the peak reported here.

It is to be noted that the qualitative feature of the dependence of G' and G'' on concentration is the same for both high and low temperatures. This demonstrates that the viscoelastic behavior of the gel state strongly depends on the nature of the high-temperature phase from which the gel phase originated. The moduli of high-temperature, low-concentration solutions are so insignificant that they are not displayed in Figures 10 and 11 within the time scales of the figures.

Conclusions

The isotropic phase is characterized viscoelastically by very little storage of energy during a cycle of deformation, while in the gel phase, the elastic response dominates the viscous flow. This gradual change of pure viscous response to more of an elastic response on going from the isotropic phase to the gel phase has been utilized in the present study to determine the phase boundaries as shown in Figure 4, while other studies on determining the phase boundaries relied upon optical microscopy and laser light scattering (static).[12,13,23-30] Recent studies by Miller et al.[38] on gels of PBLG in other solvents such as DMF and toluene predict the rheological properties to be independent of concentration and temperature. In the present study, PBLG in benzyl alcohol showed a pronounced dependence of viscoelastic properties on concentration and temperature. The most important feature of Figure 10 is that the moduli of the gel phase go through a maximum as the concentration is increased in an analogous manner to the high-temperature system. Thus the elastic behavior of the gel phase depends very strongly on the nature of the high-temperature phase from which the gel is prepared. The same concentration behavior is observed at all frequencies covered in this study (see Figure 12). As described in the previous sections, the other important feature of this system is that the viscoelastic behavior of PBLG–BA gels is time dependent, and hence kinetically controlled mechanisms dominate the gel behavior. The emergence of such mechanisms and their origins are difficult to theorize. Our current studies on this system involve cooperative diffusion measurements from dynamic light scattering experiments, and in a future publication we will discuss these light scattering results in conjunction with the present information on the rheological behavior and the available theories.

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Carrier Transport and Generation Processes in Polymer Electrolytes Based on Poly(ethylene oxide) Networks

Masayoshi Watanabe,* Masashi Itoh, Kohei Sanui, and Naoya Ogata

Department of Chemistry, Sophia University, Chiyoda-ku, Tokyo 102, Japan.
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ABSTRACT: Carrier transport and generation processes were investigated in polymer electrolytes based on poly(ethylene oxide) networks in rubbery and amorphous states. The Williams–Landel–Ferry (WLF) plots of the ionic conductivity gave a master curve irrespective of the kinds of incorporated salts, and the WLF parameters obtained were comparable to the universal values for the relaxation times of many amorphous polymers. The ionic transport did not occur by itself; segmental motion with associated carrier ions caused the ionic transport. The ionic conductivity at constant reduced temperatures tended to decrease with increasing lattice energies of the incorporated salts. The increase in the conductivity as a function of the salt concentration at constant reduced temperatures was smaller than that expected by the complete dissociation of the salt. All of the incorporated salt did not function as carrier ions, and the ion dissociation was suppressed with increasing lattice energies and concentration of the salts.

Introduction

Solid solutions of salts in polymers are new kinds of electrolytes. Much interest has been focused on the high ionic conductivity of these polymer electrolytes in terms of a fundamental understanding of fast ion transport in polymers[1] and their potential application as solid electrolytes in primary or secondary high-energy-density batteries.[2,3]

Polymer complexes consisting of linear poly(ethylene oxide) (PEO) and alkali metal salts are prototypes of solvent-free polymer electrolytes.[4] The PEO complexes have, in general, multiphase nature, which consists of a salt-rich crystalline phase, a pure PEO crystalline phase, and an amorphous phase with dissolved salt. It has been revealed that the ionic conduction takes place primarily in the amorphous phase.[5] The phase diagram is affected by many factors, such as salt species and concentration, temperature, and preparative method. Thus, the ion-conducting behavior in PEO is complicated by the change in the phase diagram with the above factors.

Amorphous PEO–salt complexes permit the investigation of ion-conducting behavior in PEO without the complication of different phases. It has been pointed out that the temperature dependence of ionic conductivity for the amorphous PEO–salt complexes obeys a WLF type equation.[6,7] This fact indicates that the ion-transport process is correlated to the viscoelastic property of the host polymers.[6,7] However, what this fact means on the molecular level is still not clear. Furthermore, the WLF-type equation does not hold in the carrier generation process but holds in the carrier transport process. Since ionic conductivity is determined by the product of the number of carrier ions and their mobility, the carrier generation process will also affect the ionic conductivity. However, little is known about the carrier generation process, for example, little is known about the number of carrier ions as functions of the incorporated salt species and concentration, and temperature.[8]

In earlier articles[9,10] we investigated the ionic conductivity of PEO network polymers with dissolved lithium perchlorate. The network structure improved the conductivity of the salt complexes by decreasing considerably the degree of crystallinity. The purpose of this study is to investigate carrier transport and generation processes in PEO in completely amorphous and rubbery states. Various kinds of alkali metal salts were incorporated in the PEO network polymers. The WLF plots of the ionic conductivity gave a master curve irrespective of the kinds of incorporated salts. The ionic conductivities at constant reduced temperatures were correlated with the lattice energies and concentration of the salts.

Experimental Section

Materials. PEO triol having a number-average molecular weight of 3.0×10^3, which was determined by OH titration, was supplied by Dai-ichi Kogyo Seiyaku Co. The PEO triol was dried under reduced pressure (10^{-3} Torr) at 80 °C for 8 h just before use. A network polymer of PEO was prepared by reaction of the PEO triol with 4-methyl-1,3-phenylene diisocyanate at 80 °C for 96 h (as shown in Figure 1). With respect to the functional groups, stoichiometric amounts of the PEO triol and isocyanate were used for the reaction. The preparative method is described elsewhere.[10] Unreacted precursors were removed from the network polymers by extraction with acetone several times. After complete evaporation of the solvent, network polymer films of about 0.3-mm thickness were obtained. The sol fraction, which could be extracted by acetone, was lower than 1 wt %. IR spectra of the network polymers showed no absorption band at 2280 cm^{-1}, assignable to –NCO groups, and a trace absorption band around 3470 cm^{-1}, assignable to –OH groups. The resulting network polymers, having a favorable mechanical strength, were colorless and transparent elastomers at room temperature. The network polymers, which had the weight swelling ratio toward water of 2.7 ± 0.1 at 30 °C, were used for the preparation of polymer electrolytes.

Various kinds of alkali metal salts were dried at appropriate temperatures (>100 °C) under reduced pressure (10^{-3} Torr) for 8 h and kept under argon atmosphere just before use. The dissolution of alkali metal salts in the network polymers was per-

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